JC02 Rec'd PCT/PTO 22 MAR 2002

FORM PTO-1390 (REV. 11-2000) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY 'S DOCKET NUMBER: 24448-0032

U S APPLICATION NO (If known, see 37 CFR 1 5): 10/088794

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/09523	September 28, 2000	September 29, 1999

TITLE OF INVENTION: Method and compositions for printing substrates

APPLICANT(S) FOR DO/EO/US: Axel Kalleder et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☑ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☐ This is an express request to begin national examination procedures (35 U S C 371(f)) The submission must include items (5), (6), (9) and (21) indicated below
4. ☑ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☑ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☑ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☑ An English language translation of the International Application as filed (35 U S C 371(c)(2)).
   a. ☑ is attached hereto.
   b. ☐ has been previously submitted under 35 U S C. 154(d)(4).
7. ☑ Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☑ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
10. ☐ An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1 97 and 1 98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3 31 is included.
13. ☑ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U S.C 1.821 - 1 825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U S C 154(d)(4).
20. ☑ Other items or information:

Express Mail Label No. EL912435826US; mailed March 22, 2002

U.S. APPLICATION NO (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/088794	PCT/EP00/09523	24448-0032

21. ☑ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

	CALCULATIONS PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**	
International preliminary examination fee (37 CFR 1 482) not paid to USPTO but international search fee (37 CFR 1 445(a)(2)) paid to USPTO **$710.00**	
International preliminary examination fee (37 CFR 1 482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	- 20 =		x **$18.00**	$
Independent claims	- 3 =		x **$80.00**	$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$270.00**	$

TOTAL OF ABOVE CALCULATIONS =	$ 890
☑ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +	$ 445
SUBTOTAL =	$ 445
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1 492(f)).	$
TOTAL NATIONAL FEE =	$ 445
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +	$ -
TOTAL FEES ENCLOSED =	$ 445
Amount to be refunded:	$
charged:	$

a. ☑ A check in the amount of $ 445 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 08-1641 in the amount of $ _____ to cover the above fees. A duplicate copy of this sheet is enclosed

c. ☑ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 08-1641 . A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public **Credit card information should not be included on this form**. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Customer Number 25213

SIGNATURE

Derek P. Freyberg

NAME

29,250

REGISTRATION NUMBER

In the Claims:

Cancel Claims 1-10, and insert therefor new Claims 11-20, to read as follows:

11. A process for the production of a printed substrate, comprising the steps of:

(i) imagewise applying to a substrate a printing paste comprising:

(1) a matrix-forming condensate comprising polyorganosiloxanes, prepared by a sol-gel process, and

(2) at least one filler selected from the group consisting of coloring, luminescent, conductive, and catalytically active fillers; and

(ii) densifying the imagewise-applied paste to form the matrix containing the at least one filler by heat treatment at a temperature below the glass transition temperature of the thus-formed matrix.

12. The process of claim 11 where the step of densifying comprises heat treatment at a temperature that is at least 200 °C below the glass transition temperature of the thus-formed matrix.

13. The process of claim 11 where the step of imagewise applying the printing paste comprises screen printing or pad printing.

14. The process of claim 11 where the substrate is a glass substrate, a glass-ceramic substrate, or a ceramic substrate, any of which optionally has been provided with a conductive coating.

15. The process of claim 11 where the printed substrate is a substrate printed with conductor tracks, spacers, or a decorative pattern.

16. A composition comprising:

(a) a matrix-forming condensate comprising polyorganosiloxanes, prepared by a sol-gel process comprising partial hydrolysis and polycondensation of:

(A) at least one organosilane of the formula $R_nSiX_{(4-n)}$, where each R is independently a non-hydrolyzable radical, each X is independently a hydrolyzable group or a hydroxy group, and n is 1, 2, or 3; or an oligomer derived therefrom,

(B) optionally, at least one hydrolyzable silane of the formula SiX_4, where each X is as defined above, and

(C) optionally, one or more compounds of glass-forming elements;

(b) at least one filler selected from the group consisting of coloring, luminescent, conductive, and catalytically active fillers;

(c) at least one organic solvent having a boiling point of at least 150 °C; and

(d) at least one rheology control agent.

17. The composition of claim 16 where the organosilane (A) comprises at least 40 mol% of the components (A) through (C) forming the condensate.

18. The composition of claim 16 where a filler is present and is selected from the group consisting of dyes, colored pigments, photoluminescent substances, electroluminescent substances, electrically conductive materials, photoconductive materials, and catalytically active fillers.

19. The composition of claim 16 where a filler is present and is a particulate conductive filler selected from the group consisting of gold, silver, copper, nickel, tungsten, molybdenum, tin oxide, indium tin oxide, lead zirconate titanate, and graphite.

20. The composition of claim 16 that is essentially free of glass particles.

REMARKS

The Amendment

Entry of this amendment is respectfully requested. No new matter is added by the amendment, because the new abstract and claims find support in the application as filed. In particular, the new abstract is in single paragraph form and the new claims remove multiple dependencies and rewrite the claims in more standard US form.

Claims 11-20 are in this application, Claims 1-10 having been canceled, and Claims 11-20 having been added by this amendment. Entry of the amendment and allowance of the claims are requested.

A copy of the Abstract, marked to show the changes, is found on the next page.

Respectfully submitted,

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March 22, 2002

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03/22/02 9 58 AM

Amended Abstract

(additions in bold, deletions between bold brackets]

ABSTRACT OF THE DISCLOSURE

[ABSTRACT OF THE DISCLOSURE

PROCESS AND COMPOSITIONS FOR PRINTING SUBSTRATES

The invention relates to a process and a composition which can be used as a printing paste**]** **Processes and compositions** for printing substrates. **[**In the process, a**]** **A** printing paste **[**comprising a)**]** **containing** a matrix-forming precondensate **[**based on**]** **containing** polyorganosiloxanes **[**which is**]** obtained by the sol-gel process, and **[**one or more colouring**]** **at least one coloring**, luminescent, conductive and/or catalytically active filler**[**s**]** is applied imagewise to the substrate and **is** densified by heat treatment**[**, where the densification is carried out**]** at a temperature **[**which is lower than**]** **below** the glass transition temperature of the **[**forming**]** matrix **being formed. The processes and printing pastes are suitable, for example, for the production of conductor tracks and decorative patterns.**

[The process and the printing pastes are suitable, for example, for the production of conductor tracks and of decorative patterns.**]**

PATENTS
Attorney Docket No. 24448-0032

EXPRESS MAIL LABEL INFORMATION – 37 CFR 1.10
Express Mail Label No.: EL912435826US; mailed March 22, 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Axel Kalleder et al. :

App. No.: (not yet known) : Art Unit: (not yet known)
Int'l App. No. PCT/EP00/09523

Filed: (herewith) : Examiner: (not yet known)
Int'l Filing Date: September 28, 2000

For: Method and compositions for printing substrates

Box PCT
Commissioner for Patents
Washington, DC 20231

Sir:

PRELIMINARY AMENDMENT

Please amend the above-identified application, before examination, as follows:

In the Abstract:

Delete the present abstract in its entirety and insert therefor a new Abstract on the following page.

Attorney Docket No. 24448-0032

Express Mail Label No. EL912435826US; mailed March 22, 2002

METHOD AND COMPOSITIONS FOR PRINTING SUBSTRATES

The invention relates to a process for the production of printed substrates in which a special printing paste is applied imagewise to a substrate and densified by heat treatment, and to compositions which are suitable for carrying out this process.

Conductive printing pastes, in particular conductive screen-printing pastes, for printing substrates with conductive components, such as, for example, conductor tracks, are, in accordance with the prior art, prepared using, generally, low-melting glass particles, for example glass frits, with admixture of conductive metal powders. To these are added further components, usually of an organic nature, which facilitate the establishment of a suitable rheology, for example a pronounced thixotropic behavior. These components are usually organic oligomers, for example fish oils, celluloses and cellulose derivatives, polyalcohols or similar substances. After application by a printing process, for example screen printing or pad printing, the printed areas are fired, during which the glass melts and a matrix forms for the percolating metal particles. Disadvantages of this method are the relatively high firing temperature of at least 600 to 700°C and the formation of a low-viscosity phase, which has the effect that the aspect ratios are relatively low, i.e. the lines are fairly broad owing to the melting behavior of the glass. In addition to the metal particles, other particles, for example colored pigments, may also be admixed with glass particles of this type.

EP-A-535374 describes the use of silanes as additives in screen-printing enamels. However, the function of these additives

consists merely in fixing the decorative prints after drying. Glass particles are employed in the printing pastes described therein.

DE-A-195 20 964 describes the composition of a sol-gel screen-printing material in which glass frits and optionally xerogel particles are employed. The starting materials used can be silicates.

The object according to the invention consisted in providing a simple and inexpensive process for the production of printed substrates using a printing paste which can be densified even at relatively low temperatures to give a stable, strongly adherent, imagewise layer, which may also be in structured form, for example in the form of conductor tracks, and by means of which line images can be produced with very high resolution. The aim here is to avoid the use of heavy-metal components for the matrix, which were hitherto necessary in order to lower the melting point of the matrix.

The abovementioned object is achieved in accordance with the invention by a process for the production of printed substrates in which a printing paste comprising a) a matrix-forming condensate based on polyorganosiloxanes which is obtained by the sol-gel process, and b) one or more coloring, luminescent, conductive and/or catalytically active fillers, is applied imagewise to the substrate and densified by heat treatment, said process being characterized in that densification is carried out at a temperature which is lower than the glass transition temperature of the matrix forming.

On use of metal powders as fillers, conductor tracks with a very high degree of densification, which are the prerequisite for high conductivity and a high degree of percolation, are, surprisingly, produced in the process according to the invention, although fluxing media are not added to the system, as in the case of the conventional use of glass particles or glass frits. The technical advantage of this process consists in that, in contrast to the prior art, melting is avoided, and the printed structures thus do not spread out. The geometry of the printed lines or image patterns is thus kept within very narrow dimensions; in the case of line images, very fine lines, for example, of high edge sharpness and with an aspect ratio which is significantly greater than that of the prior art are achieved. If other fillers are used instead of the metallic conductors preferably employed, decorative patterns and lines or areas can thus also be produced by printing. In a similar manner, embossed or extruded structures can be produced.

The substrates employed in the process according to the invention can be any desired heat-resistant materials, for example metals, alloys, plastics, ceramic, glass-ceramic or glass. Preferred substrates are ceramic, glass-ceramic and glass. The substrate may also be pre-coated. In particular in the case of applications in which conductive fillers are employed, for example for the production of conductor tracks, use is preferably made of substrates having a conductive coating, in particular glass having a conductive coating. The substrates or glass substrates having a conductive coating are known in the art and are commercially available. The coating may be, for example, tin oxide or indium tin oxide (ITO). In the

process according to the invention, the substrate serves as print carrier, to which the image pattern is applied.

Suitable printing processes are generally all processes in which printing pastes are employed. Preference is given to screen printing, offset printing and pad printing.

The process according to the invention is particularly suitable for printing substrates with conductive components, as used, for example, for the production of conductor tracks. Conductive printing pastes containing conductive fillers as a component are employed for this purpose. Corresponding fillers are explained in greater detail below.

The printing paste is applied imagewise to the substrate. The term "imagewise" here means that the printing paste is not applied as a full-area layer, but instead in any desired pattern. Owing to the high resolution that can be achieved therewith, the process according to the invention is particularly suitable for the production of very fine patterns.

After the printing paste has been applied to the substrate, it is optionally dried, for example at temperatures of from 80 to 200°C.

The printing paste is preferably densified by heat treatment, preferably after drying. During the densification, the printed structures are not melted, but instead the heat treatment is carried out at a temperature which is lower than the glass transition temperature of the matrix forming. The heat treatment is preferably carried out at a temperature which is at least 200°C, preferably at least 400°C, lower than the glass

transition temperature of the matrix forming. Depending on the matrix forming (for example SiO_2), the firing temperature may be as much as from 600 to 700°C below the glass transition temperature.

The heat treatment is preferably carried out at temperatures in the range from 400°C to 800°C, more preferably from 450°C to 600°C.

The printing paste employed in accordance with the invention comprises a matrix-forming condensate based on polyorganosiloxanes which is obtained by the sol-gel process. The sol-gel process is a process which is known in the art. In accordance with the invention, partial hydrolysis and polycondensation of the hydrolysable compounds, in particular hydrolysable silanes, gives a condensate which is not yet fully condensed (precondensate). The degree of condensation is, for example, from 20 to 80%, preferably from 40 to 60%. The liquid sol obtained in this way is employed for the preparation of the printing paste. The further condensation takes place during later drying or densification.

The matrix-forming condensate based on polyorganosiloxanes is obtainable, for example, by partial hydrolysis and polycondensation of:

(A) at least one organosilane of the general formula (I)

$$R_nSiX_{(4-n)} \qquad (I)$$

in which the radicals X are identical or different and are hydrolysable groups or hydroxyl groups, R is identical or different and is a non-hydrolysable radical, and n is 1, 2 or 3, or an oligomer derived thereof,

(B) optionally at least one hydrolysable silane of the general

formula (II)

$$SiX_4 \qquad (II)$$

in which X is as defined above, and

(C) optionally one or more compounds of glass- or ceramic-forming elements.

In the organosilanes of the formula (I) and the hydrolysable silanes of the formula (II), the hydrolysable groups X are, for example, hydrogen or halogen (F, Cl, Br or I), alkoxy (preferably C_{1-6}-alkoxy, such as, for example, methoxy, ethoxy, n-propoxy, i-propoxy and butoxy), aryloxy (preferably C_{6-10}-aryloxy, such as, for example, phenoxy), acyloxy (for example C_{1-6}-acyloxy, such as, for example, acetoxy or propionyloxy), alkylcarbonyl (preferably C_{2-7}-alkylcarbonyl, such as, for example, acetyl), amino, monoalkylamino or dialkylamino, preferably having from 1 to 12, in particular from 1 to 6, carbon atoms.

R is a non-hydrolysable organic radical, which may optionally carry a functional group. Examples of R are alkyl (preferably C_{1-6}-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl and t-butyl, pentyl, hexyl or cyclohexyl), alkenyl (preferably C_{2-6}-alkenyl, such as, for example, vinyl, 1-propenyl, 2-propenyl and butenyl), alkynyl (preferably C_{2-6}-alkynyl, such as, for example, acetylenyl and propargyl), and aryl (preferably C_{6-10}-aryl, such as, for example, phenyl and naphthyl).

Specific examples of functional groups of the radical R are the epoxy, hydroxyl, ether, amino, monoalkylamino, dialkylamino, amide, carboxyl, mercapto, thioether, vinyl, acryloxy, methacryloxy, cyano, halogen, aldehyde, alkylcarbonyl, sulfonic

acid and phosphoric acid groups. These functional groups are bonded to the silicon atom via alkylene, alkenylene or arylene bridging groups, which may be interrupted by oxygen or sulfur atoms or -NH- groups. The said bridging groups are derived, for example, from the above-mentioned alkyl, alkenyl or aryl radicals. The radicals R preferably contain from 1 to 18, in particular from 1 to 8, carbon atoms. The said radicals R and X may optionally have one or more conventional substituents, such as, for example, halogen or alkoxy.

In the general formula (I), n has the value 1, 2 or 3, preferably the value 1 or 2.

Particularly preferred hydrolysable silanes of the formula (II) are tetraalkoxysilanes, such as tetraethoxysilane (TEOS). Particularly preferred organosilanes of the formula (I) are epoxysilanes, such as 3-glycidyloxypropyltrimethoxysilane (GPTS), and monoalkyltrialkoxysilanes, such as methyltriethoxysilane (MTEOS).

The condensate may be prepared entirely from one or more organosilanes of the formula (I). If these organosilanes contain a functional group, this is also a preferred embodiment. In accordance with the invention, the condensate is prepared using at least 40 mol%, preferably at least 60 mol%, of the organosilane of the general formula (I). If the organosilane employed does not contain any functional groups, hydrolysable silanes of the formula (II) are preferably also employed. The condensate can be prepared using up to 60 mol%, preferably not more than 40 mol%, of hydrolysable silanes of the general formula (II).

If desired, the condensate can be prepared additionally using one or more compounds of glass- or ceramic-forming elements. These are preferably soluble or dispersible in the reaction medium. It is possible to use, for example, compounds (halides, alkoxides, carboxylates, chelates, etc.) of lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, boron, aluminum, titanium, zirconium, tin, zinc or vanadium.

The hydrolysis and polycondensation are either carried out in the absence of a solvent or preferably in an aqueous or aqueous/organic reaction medium, optionally in the presence of an acidic or basic condensation catalyst, such as HCl, HNO_3 or NH_3. In the case of the use of a liquid reaction medium, the starting components are soluble in the reaction medium. Suitable organic solvents are, in particular, water-miscible solvents, for example monohydric or polyhydric aliphatic alcohols, ethers, esters, ketones, amides, sulfoxides and sulfones.

The hydrolysis and polycondensation are optionally carried out in the presence of a complexing agent, for example nitrates, β-dicarbonyl compounds (for example acetylacetonates or acetoacetates), carboxylic acids (for example methacrylic acid) or carboxylates (for èxample acetate, citrate or glycolate), betaines, diols, diamines (for example DIAMO) or crown ethers.

Besides the abovementioned sol (precondensate), the printing paste also comprises one or more coloring, luminescent, conductive and/or catalytically active fillers. These are preferably particles in the form of a powder having dimensions in the µm range (for example up to 30 µm) or in the sub-µm

range. They may be, for example, spherical, lamellar or irregularly shaped bodies. The coloring fillers are, in particular, dyes and colored pigments. The luminescent fillers include, for example, photo- and electro-luminescent substances. The conductive fillers are, in particular, electrically conductive and/or photoconductive materials. Catalytically active fillers are, for example, aluminum oxides, chromium oxides and titanium oxides. In the case of the conductive fillers, the printing paste preferably comprises from 50 to 80% by weight, particularly preferably from 70 to 75% by weight, of these fillers. If conductive fillers are employed, the densified printing paste printed onto the carrier comprises at least 80% by weight, preferably at least 95% by weight, of fillers. If only coloring fillers are used, significantly lower proportions, for example less than 10% by weight, may be present in the printing paste to be applied, depending on the coloring power and the desired color effect.

Examples of materials which can be employed as conductive fillers are metals and metal oxides, but also other elements or element compounds, for example aluminum, gold, silver, copper, nickel, chromium, molybdenum, tungsten, tin oxide, indium tin oxide, lead zirconate titanate and graphite.

Coloring fillers which can be used are inorganic or organic substances which remain stable even at the densification temperatures. Suitable heat-resistant dyes are, for example, azo dyes, such as Methyl Orange, Alizarin Yellow or Congo Red; dispersion dyes, such as Disperse Red; triphenylmethane dyes, such as Malachite Green, eosine, fluorescein, aurine and phenolphthalein; vat dyes, such as indigo, thioindigo and

anthraquinone dyes; perylene dyes; and fluorescent dyes, such as Fluorescent Brightener 28. Pigments which can be used are, for example, mica-based pigments (Iriodin), phthalocyanines with, for example, Cu, Co, Ni, Zn or Cr as the central atom; carbon black pigments and TiO_2.

The printing paste may optionally also comprise nanoscale particles, for example metal colloids of Ag, Au, Cu, Pd and Pt, or metal compounds, for example (optionally hydrated) oxides, such as ZnO, CdO, SiO_2, TiO_2, ZrO_2, CeO_2, SnO_2, Al_2O_3, In_2O_3, La_2O_3, Fe_2O_3, Cr_2O_3, CuO, Cu_2O, Mn_2O_3, Ta_2O_5, Nb_2O_5, V_2O_5, PdO, MoO_3 or WO_3; chalcogenides, such as, for example, sulfides (for example CdS, ZnS, PbS and Ag_2S), selenides (for example GaSe, CdSe and ZnSe) and tellurides (for example ZnTe or CdTe), halides, such as AgCl, AgBr, AgI, CuCl, CuBr, CdI_2 and PbI_2; carbides, such as CdC_2 or SiC; arsenides, such as AlAs, GaAs and GeAs; antimonides, such as InSb; nitrides, such as BN, AlN, Si_3N_4 and Ti_3N_4; phosphides, such as GaP, InP, Zn_3P_2 and Cd_3P_2; phosphates, silicates, zirconates, aluminates, stannates and the corresponding mixed oxides (for example those having a perovskite structure, such as $BaTiO_3$ and $PbTiO_3$).

The nanoscale filler particles generally have a particle size in the range from 1 to 100 nm, preferably from 2 to 50 nm and particularly preferably from 5 to 20 nm. These materials can be employed either in the form of a powder or preferably in the form of a (in particular acid-stabilized) sol.

The amount of the coloring, luminescent and/or catalytically active filler depends on the desired functional properties of the coating, for example the desired color intensity.

The composition according to the invention which can be used as printing paste furthermore comprises one or more high-boiling organic solvents having a boiling point of at least 150°C, preferably at least 180°C, particularly preferably at least 200°C, in an amount of, in general, up to 50% by weight, for example from 1 to 30% by weight or from 1 to 10% by weight.

Preferred examples of suitable high-boiling organic solvents are di-, tri-, tetra-, penta- or hexamers of monoglycols, such as, for example, the di-, tri-, tetra-, penta- or hexamers of ethylene glycol, propylene glycol or butylene glycol, and mono- or diethers thereof, in which one or both hydroxyl groups may be replaced by, for example, a methoxy, ethoxy, propoxy or butoxy group; terpenes, for example terpineol; and polyols, for example 2-methyl-2,4-pentanediol. Especial high-boiling solvents are polyethylene glycols and ethers thereof, such as diethylene glycol, triethylene glycol and tetraethylene glycol, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether or diethylene glycol monobutyl ether. Of these, particular preference is given to diethylene glycol, tetraethylene glycol and diethylene glycol monobutyl ether. It is of course also possible to employ mixtures of two or more of these solvents.

The composition according to the invention which can be used as printing paste furthermore comprises one or more rheology control agents in an amount of preferably not more than 5% by weight, for example from 0.5 to 2% by weight. The rheology control agent serves to adjust the structural viscosity or the thixotropy of the printing pastes. Use can be made here of the rheology control agents usually used in accordance with the

prior art. Examples of rheology control agents of this type are fish oils, celluloses, cellulose derivatives and polyalcohols.

The composition may additionally comprise conventional additives for printing pastes. However, the printing paste preferably comprises essentially no glass particles or glass frits that are usually employed in accordance with the prior art, which serve as matrix formers. This is because, surprisingly, the matrix-forming function is, in accordance with the invention, taken on by the (pre)condensate employed, in addition to its function as binder. Special glass particles which do not function as matrix former but instead, for example, serve as spacer and are therefore not melted, may, by contrast, be present in the composition used in accordance with the invention.

The components are combined and formed into a paste by methods known to the person skilled in the art, for example by mixing or compounding using a roll mill or a ball mill. Methods likewise known to the person skilled in the art are used to set the viscosity which is suitable for printing, for example with the aid of a rheology control agent.

The process according to the invention and the composition according to the invention are particularly suitable for the production of conductor tracks, for example very fine conductor tracks having widths of less than 100 µm and heights of up to 30 µm on glass, glass-ceramic and ceramic substrates, which can be used, in particular, for display technology and for photovoltaic applications. However, the process according to the invention and the composition according to the invention are also suitable for decorative applications, with high resolutions and thus the formation of very fine lines being possible.

EXAMPLES

EXAMPLE 1: Preparation of a conductive screen-printing paste based on γ-glycidyloxypropyltrimethoxysilane (GPTS)

473.25 g of γ-GPTS are mixed with 54.18 g of water and refluxed for 24 hours. The methanol liberated in the hydrolysis or alcoholysis (116.28 g) is removed in a rotary evaporator. The GPTS prehydrolysate prepared in this way is employed for the preparation of a printing paste. 38.0 g of silver powder (of which 19.0 g are lamellar silver powder > 20 µm and 19.0 g are silver powder from 1.5 to 2.5 µm) are mixed with 2.375 g of the GPTS prehydrolysate. 0.076 g of hydroxypropylcellulose (average molecular weight 100 000 g/mol) dissolved in 5.82 g of tetraethylene glycol is added.

The resultant mixture can be formed into a paste in a roll mill or with the aid of a ball mill. Application takes place using the parameters (for example doctor blade speed up to a maximum of 60 cm/s) and materials (for example stainless steel sieve 325 mesh, silicone doctor blade) which are usual in screen printing. The densification is carried out at a temperature of greater than 450°C.

EXAMPLE 2: Preparation of a decorative screen-printing paste based on γ-glycidyloxypropyltrimethoxysilane (GPTS)

The GPTS prehydrolysate is prepared as described in Example 1.

4.0 g of TiO_2 (Merck 808), 0.5 g of tetraethylene glycol and, in order to provide thixotropy, 0.02 g of hydroxypropylcellulose

(average molecular weight 100 000 g/mol) dissolved in 0.94 g of terpineol are added to 2.37 g of this prehydrolysate.

The conversion into a paste and the application are carried out as in Example 1.

EXAMPLE 3: Preparation of a screen-printing paste based on an organically modified, inorganic binder

A mixture of 62.3 g of methyltriethoxysilane (MTEOS) and 21.68 g of tetraethoxysilane (TEOS) is initially introduced. 35.18 g of silica sol (Levasil 300/30) and 0.63 ml of concentrated hydrochloric acid are added with vigorous stirring. The mixture is hydrolyzed for 15 minutes in an ice bath. 75.0 g of terpineol are added to the mixture prepared in this way. After the mixture has been stirred for 15 minutes, the ethanol present in the mixture (58.94 g) is evaporated in a rotary evaporator.

1.3 g of Iriodin Silk Red WR2 and 0.1 ml of M50 silicone oil are added to 2.5 g of this mixture. In order to provide thixotropy, 0.2 g of ethylcellulose (average molecular weight 20 000 g/mol) dissolved in 1.8 g of terpineol are added.

The application is carried out as in Example 1.

WHAT IS CLAIMED IS:

1. A process for the production of printed substrates, in which a printing paste comprising a) a matrix-forming condensate based on polyorganosiloxanes which is obtained by the sol-gel process, and b) one or more coloring, luminescent, conductive and/or catalytically active fillers, is applied imagewise to the substrate and densified by heat treatment, said process being characterized in that densification is carried out at a temperature which is lower than the glass transition temperature of the matrix forming.

2. A process according to Claim 1 wherein the densification is carried out at a temperature which is at least 200°C lower than the glass transition temperature of the matrix forming.

3. A process according to Claim 1 or 2 wherein the printing paste is applied to the substrate by screen printing or pad printing.

4. A process according to one of Claims 1 to 3 wherein the substrate used is a glass, glass-ceramic or ceramic substrate which has optionally been provided with a conductive coating.

5. A process according to one of Claims 1 to 4 wherein conductor tracks or spacers, in particular for display technology and for photovoltaic applications, or decorative patterns are printed on.

6. A composition comprising

a) a matrix-forming condensate based on polyorganosiloxanes which is obtained by the sol-gel process, obtainable by partial hydrolysis and polycondensation of

(A) at least one organosilane of the general formula (I)

$$R_nSiX_{(4-n)} \qquad (I)$$

in which the radicals X are identical or different and are hydrolysable groups or hydroxyl groups, R is identical or different and is a non-hydrolysable radical, and n is 1, 2 or 3, or an oligomer derived therefrom,

(B) optionally at least one hydrolysable silane of the general formula (II)

$$SiX_4 \qquad (II)$$

in which X is as defined above, and

(C) optionally one or more compounds of glass- or ceramic-forming elements,

b) one or more coloring, luminescent, conductive and/or catalytically active fillers,

c) one or more high-boiling organic solvents having a boiling point of at least 150°C, and

d) one or more rheology control agents.

7. A composition according to Claim 6 wherein the condensate has been prepared using at least 40 mol% of the organosilane of the general formula (I).

8. A composition according to Claim 6 or 7 wherein one or more fillers from the group consisting of dyes, colored pigments, photo- or electro-luminescent substances,

electrically conductive or photoconductive materials and catalytically active fillers are present.

9. A composition according to one of Claims 6 to 8 wherein the conductive filler comprises particles of gold, silver, copper, nickel, tungsten, molybdenum, tin oxide, indium tin oxide, lead zirconate titanate or graphite.

10. A composition according to one of Claims 6 to 9 wherein it is essentially free from glass particles.

ABSTRACT OF THE DISCLOSURE

PROCESS AND COMPOSITIONS FOR PRINTING SUBSTRATES

The invention relates to a process and a composition which can be used as a printing paste for printing substrates. In the process, a printing paste comprising a) a matrix-forming precondensate based on polyorganosiloxanes which is obtained by the sol-gel process, and b) one or more coloring, luminescent, conductive and/or catalytically active fillers, is applied imagewise to the substrate and densified by heat treatment, where the densification is carried out at a temperature which is lower than the glass transition temperature of the matrix forming.

The process and the printing pastes are suitable, for example, for the production of conductor tracks and of decorative patterns.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☐ Declaration Submitted with Initial Filing **OR** ☒ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	24448-0032
First Named Inventor	Axel KALLEDER
COMPLETE IF KNOWN	
Application Number	10/088,794
Filing Date	3/22/02
Art Unit	
Examiner Name	

As the below named inventor, I hereby declare that:

My residence, mailing address, and citizenship are as stated below next to my name.

I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD AND COMPOSITIONS FOR PRINTING SUBSTRATES

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☑ was filed on (MM/DD/YYYY) 09/28/2000 as United States Application Number or PCT International Application Number PCT/EP00/09523 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
199 46 712.9	Germany	09/29/1999	☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

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DECLARATION — Utility or Design Patent Application

Direct all correspondence to: ☐ Customer Number or Bar Code Label 25213 OR ☐ Correspondence address below

Name

Address

City | State | ZIP

Country | Telephone | Fax

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

NAME OF SOLE OR FIRST INVENTOR : ☐ A petition has been filed for this unsigned inventor

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☐ Additional inventors are being named on the 1 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto.

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DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet
Page 1 of 1

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor		
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Residence: City:	State:	Country:	Citizenship:
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Burden Hour Statement This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

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PATENTS
Attorney Docket No. 24448-0032

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

First Inventor Name: Axel KALLEDER

PCT Int'l. App. No.: PCT/EP00/09523

Int'l. Filing Date: September 28, 2000

For: METHOD AND COMPOSITIONS FOR PRINTING SUBSTRATES

Commissioner for Patents
Washington, D.C. 20231

Sir:

POWER OF ATTORNEY BY ASSIGNEE AND STATEMENT UNDER 37 CFR 3.73

Institut für Neue Materialien gemeinnützige GmbH ("INM"), a German corporation, states that it is the assignee of the entire right, title and interest in the US national phase of the PCT International Application identified above by virtue of an assignment from the inventors, a copy of which is attached hereto.

As assignee of record of the entire interest of the above identified application, INM hereby appoints the practitioners at Customer Number 25213 as its attorneys and agents to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

The undersigned are authorized to act on behalf of the assignee.

Institut für Neue Materialien gemeinnützige GmbH

By: [signature] Date: April 02, 2002
Helmut Schmidt
Managing Director

By: [signature] Date: April 08, 2002
Werner Bonke
Business Director

ASSIGNMENT Attorney Docket No. 24448-0032

WHEREAS, We, Axel KALLEDER, Rainer KREUTZER, Martin MENNIG and Helmut SCHMIDT, having the addresses indicated below, are joint inventors of certain subject matter entitled
METHOD AND COMPOSITIONS FOR PRINTING SUBSTRATES
(the "Invention"), for which a patent is sought as the US national phase of PCT International Application No. PCT/EP00/09523 filed September 28, 2000;

AND WHEREAS, Institut fuer Neue Materialien gemeinnuetzige GmbH, having an address at Im Stadtwald, Gebaeude 43, 66123 Saarbruecken, Germany ("INM") desires to perfect its right to the Invention and in the Letters Patent to be obtained therefor from the United States of America;

NOW, THEREFORE, in exchange for good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, We acknowledge INM's interest in the Invention and hereby assign to INM for the United States of America all our rights, title and interest in the Invention, as described and claimed in the US national phase of PCT International Application No. PCT/EP00/09523 filed September 28, 2000; or in any continuation, division, reissue, reexamination or extension thereof; the Invention, application and Letters Patent to be owned by INM, their successors, assigns and legal representatives, to the full end of the term for which such Letters Patent may be granted.

This assignment is effective as of September 28, 2000.

ASSIGNMENT Attorney Docket No. 24448-0032

We have read and understand this Assignment document for the patent sought as the US national phase of PCT International Application No. PCT/EP00/09523 filed Setember 28, 2000 and agree thereto, as indicated by our signature as set forth below.

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